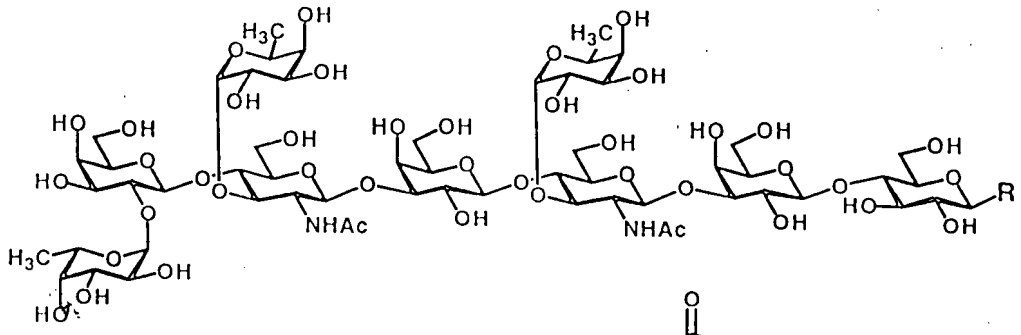
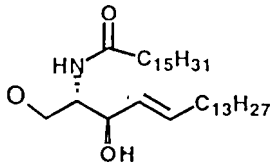
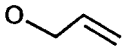
Figure 1.



KH-1 Antigen (1) R =

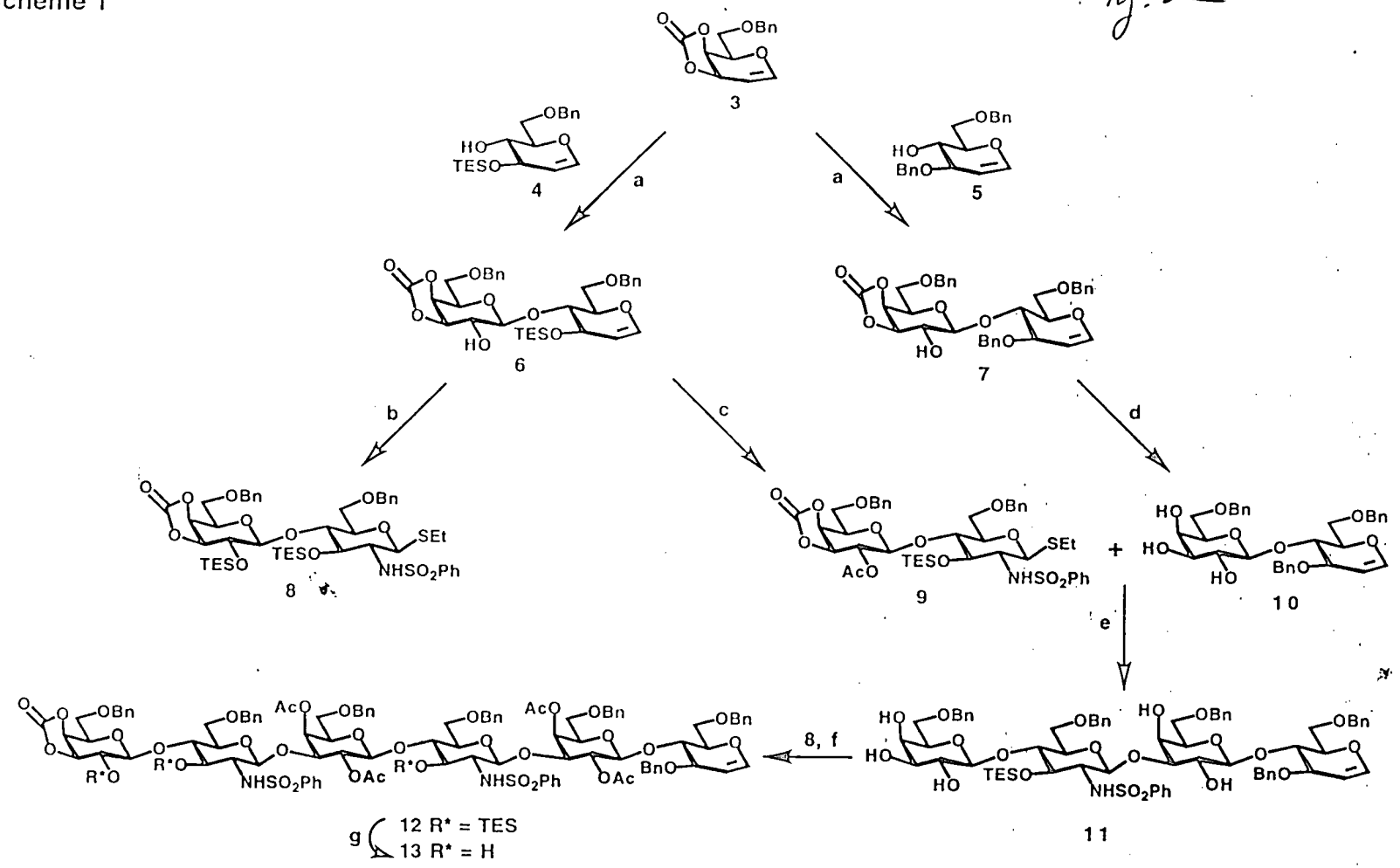


Bioconjugatable analog (2) R =



Scheme 1[a]

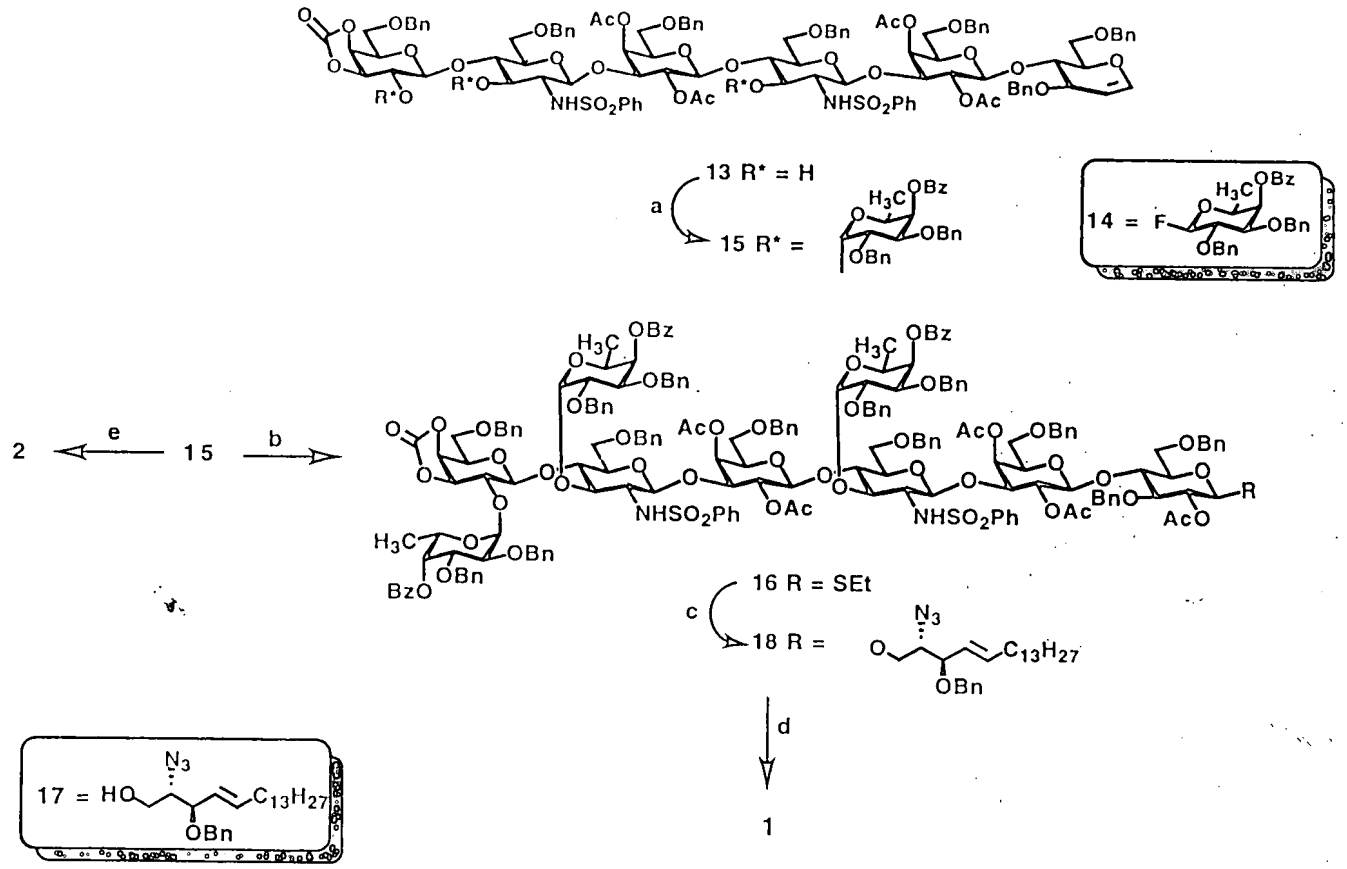
Fig. 2



[a] Reagents: (a) (i) 3,3-dimethyldioxirane, CH_2Cl_2; (ii) 4 or 5, $ZnCl_2$, THF 65% for 6 & 55% for 7; (b) (i) TESOTf, Et_3N, CH_2Cl_2, 92%, (ii) $I(coll)_2ClO_4$, $PhSO_2NH_2$, 4 Å molecular sieves, CH_2Cl_2, > 90%; (iii) LHMDS, EtSH, DMF > 90% (c) (i) Ac_2O, Et_3N, DMAP, CH_2Cl_2, 95%; (ii) $I(coll)_2ClO_4$, $PhSO_2NH_2$, 4 Å molecular sieves, CH_2Cl_2, > 90%; (iii) LHMDS, EtSH, DMF (iv) Ac_2O, Et_3N, DMAP, CH_2Cl_2, 85%; (d) K_2CO_3, MeOH 80%; (e) (i) MeOTf, di-*t*-butylpyridine, Et_2O:CH_2Cl_2 (2:1), 4 Å MS (55%), (ii) K_2CO_3, MeOH (85%); (f) (i) MeOTf, di-*t*-butylpyridine, Et_2O:CH_2Cl_2 (2:1), 4 Å MS (60%); (ii) Ac_2O, Py, DMAP, CH_2Cl_2 (95%); (g) TBAF:AcOH (93%).

Scheme 2[a]

Fig. 3



[a] Reagents: (a) **14**, $Sn(OTf)_2$, Tol:THF(10:1), 4 Å MS (60%); (b) (i) 3,3-dimethyldioxirane, CH_2Cl_2; (ii) EtSH, CH_2Cl_2, H^+ (cat); (iii) Ac_2O, Py, CH_2Cl_2 60% (3 steps) (c) **17**, MeOTf, Et_2O:CH_2Cl_2 (2:1), 4 Å MS (55%); (d) (i) Lindlar's catalyst, H_2, palmitic anhydride, EtOAc, 85% (ii) Na, NH_3, THF; (MeOH quench); (iii) Ac_2O, Et_2N, DMAP, CH_2Cl_2 (iv) MeONa, MeOH, 70% (3 steps); (e) (i) Na, NH_3, THF; (MeOH quench); (ii) Ac_2O, Et_3N, DMAP, CH_2Cl_2; (iii) 3,3-dimethyldioxirane, CH_2Cl_2; (iv) Allyl Alcohol (v) MeONa, MeOH, 60%..

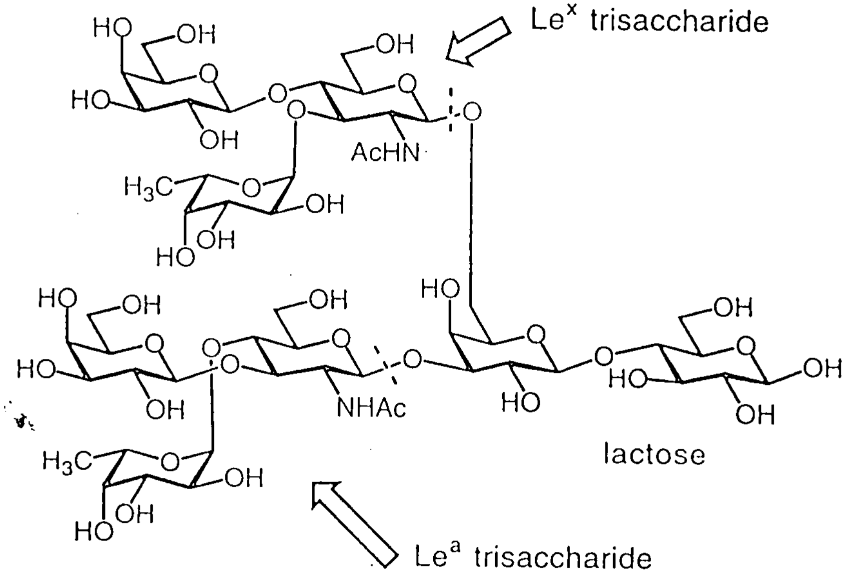
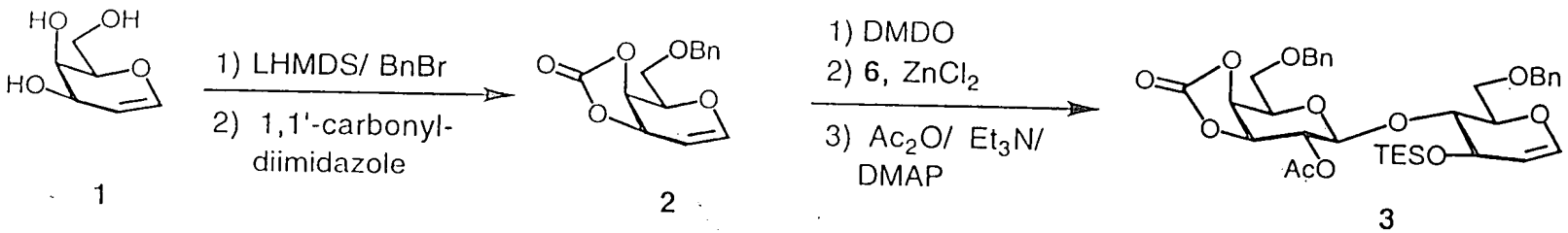


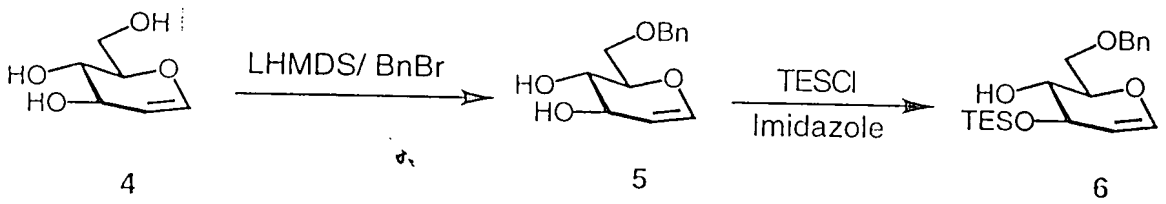
Fig. 4

Donor for Le^x Part

Fig. 5



* DMDO: dimethyldioxirane



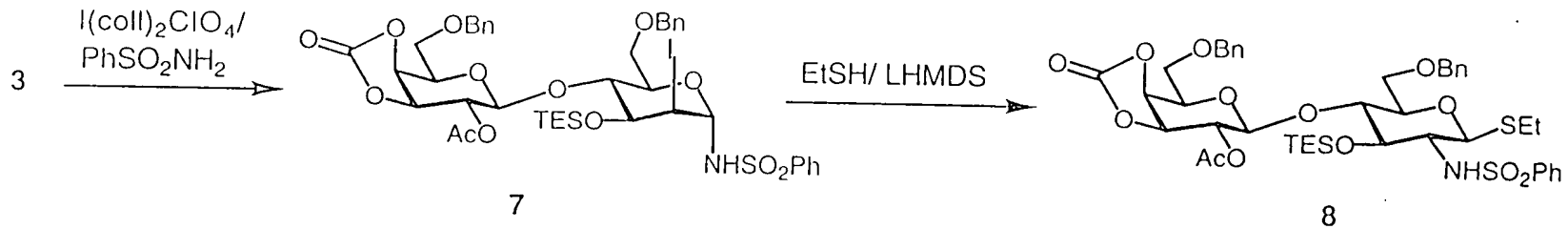
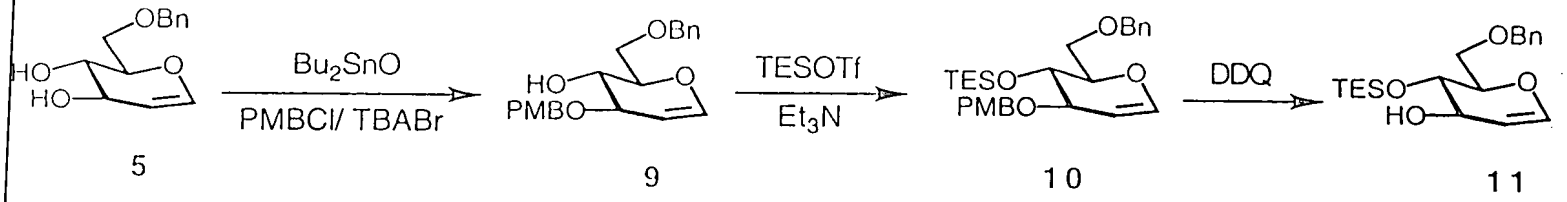
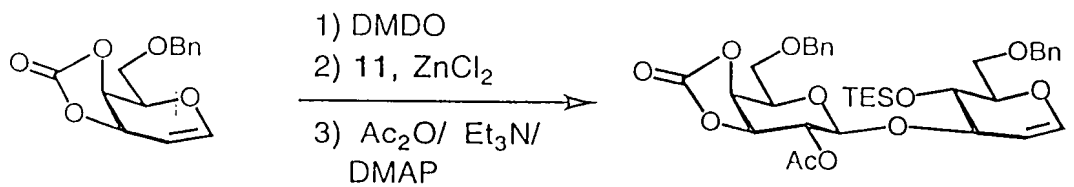


Fig. 6

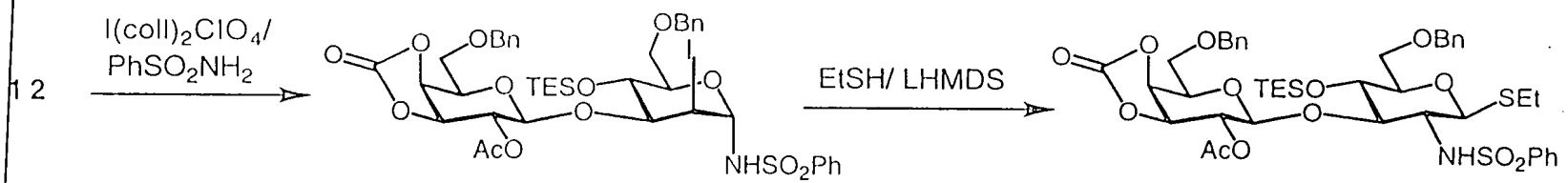
Donor for Le^a Part



5 9 10 11



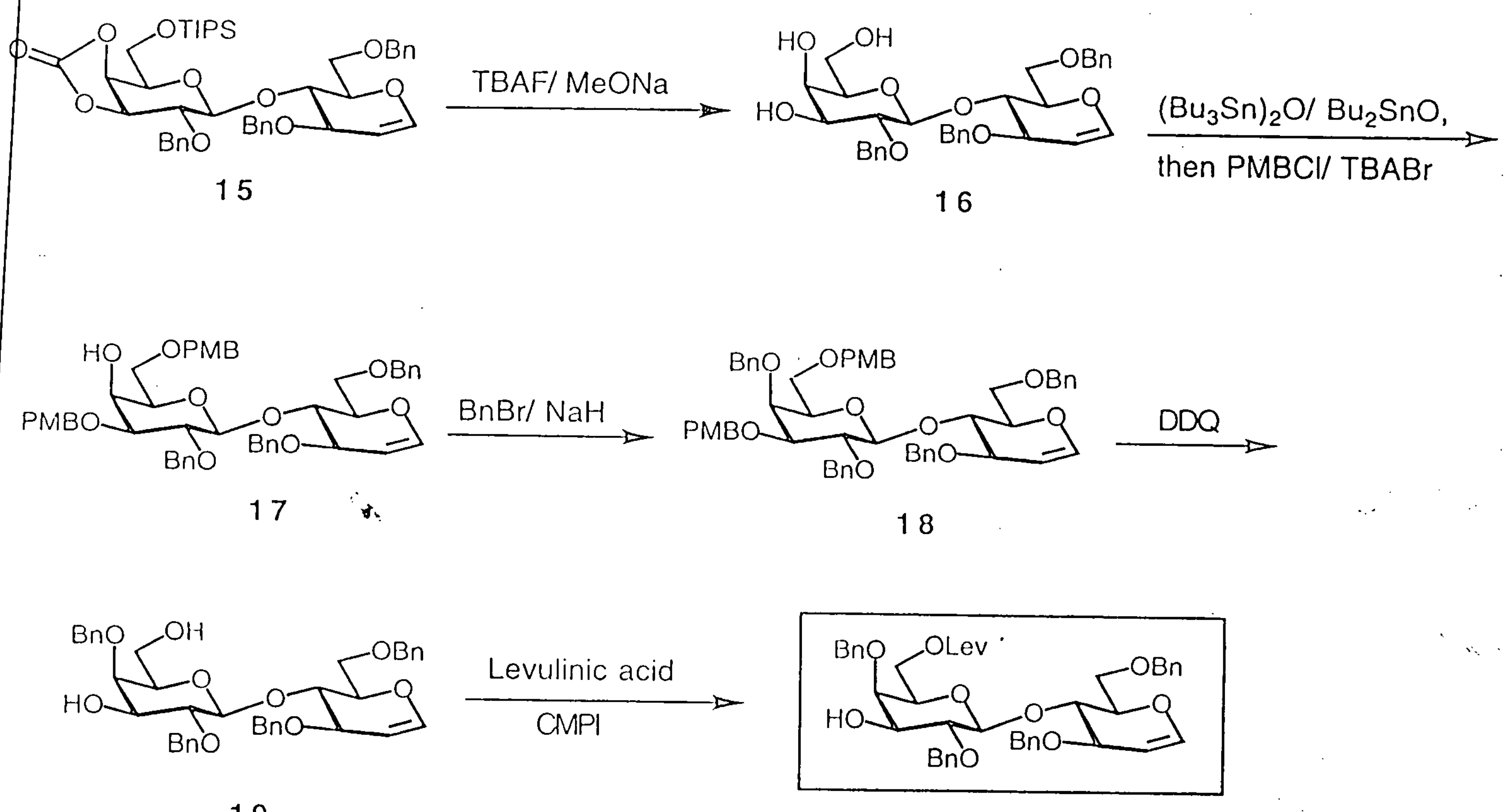
2 12



13 14

Acceptor for N3 Antigens

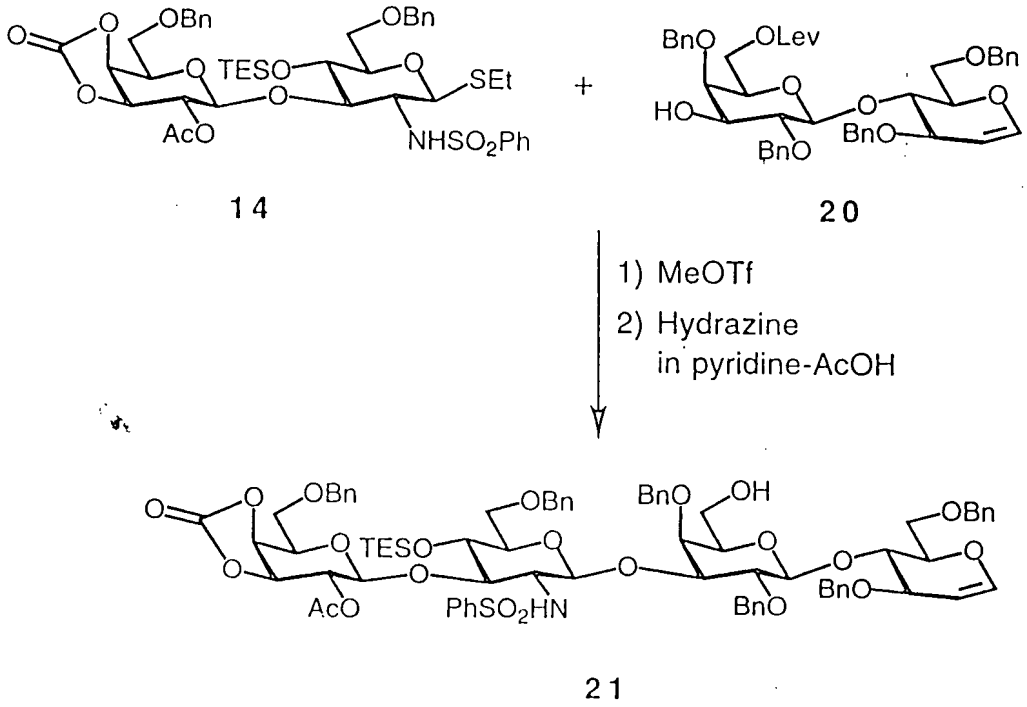
Fig 7



*CMPI: 2-Chloromethyl pyridinium iodide

Fig. 8

2 + 2 Coupling for Major N3 Antigen



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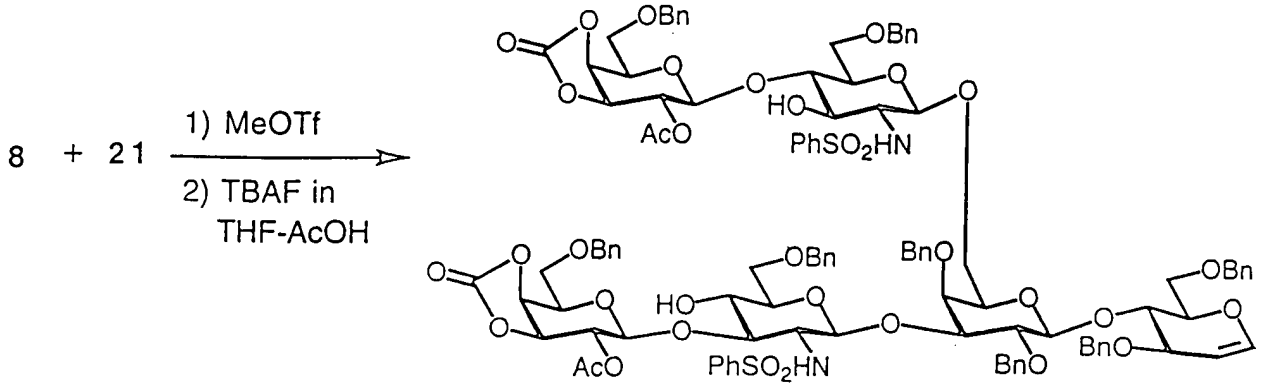
21

2 + 4 and +1,1 Coupling



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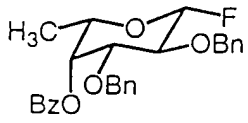

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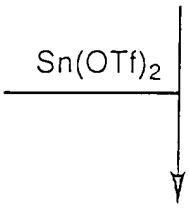

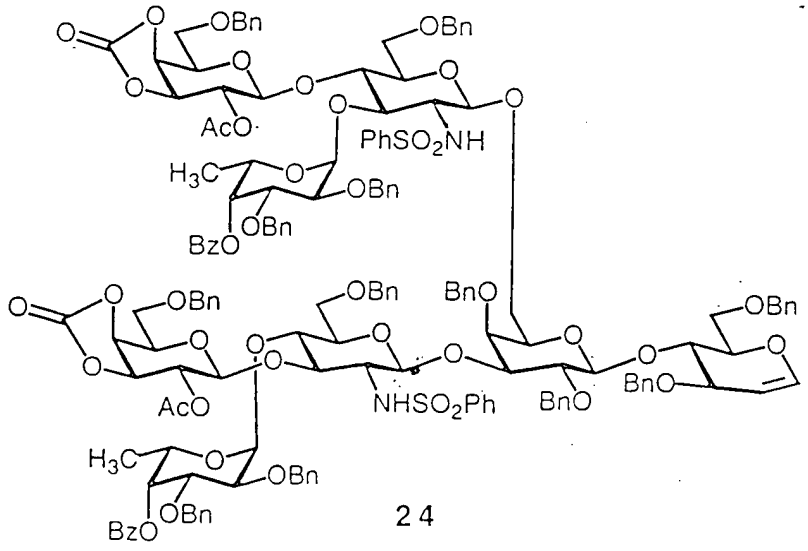

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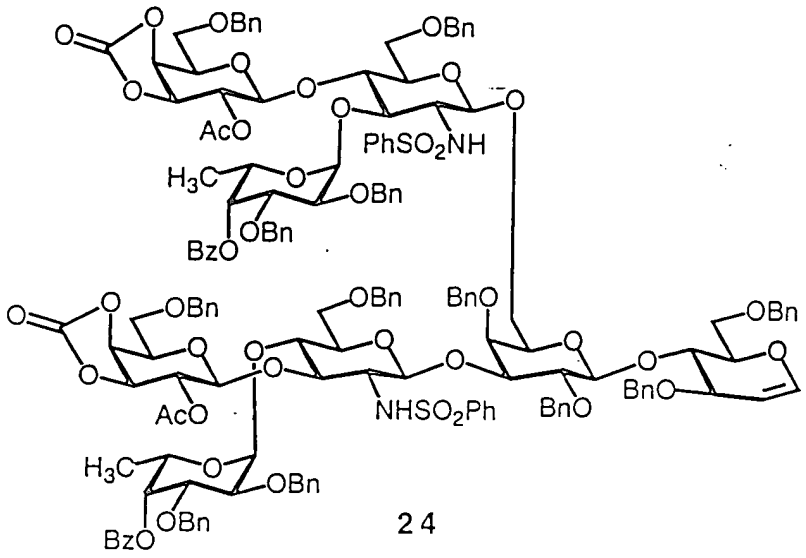
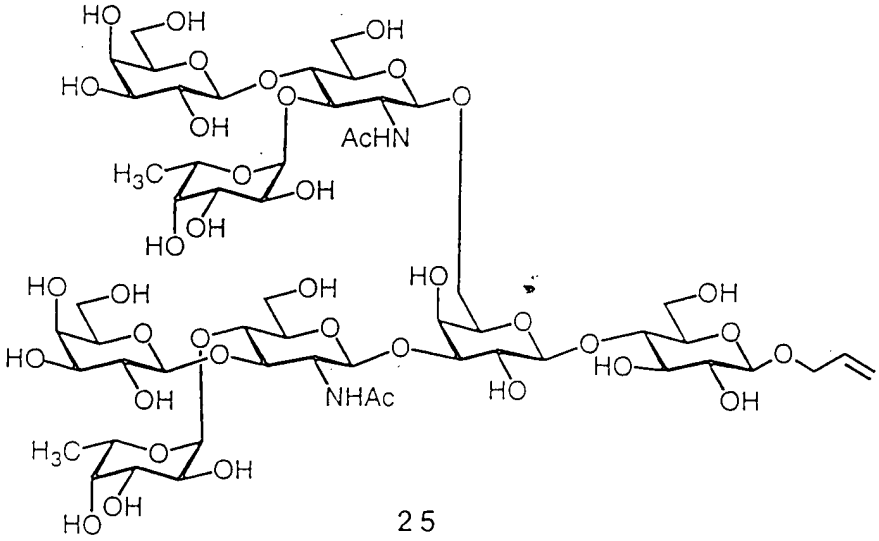
Deprotection for *major*-N3 Epitope



24

1) Na/ NH_3, then
Ac_2O/ Et_3N/ DMAP
2) DMDO, then allyl alcohol
3) NaOMe



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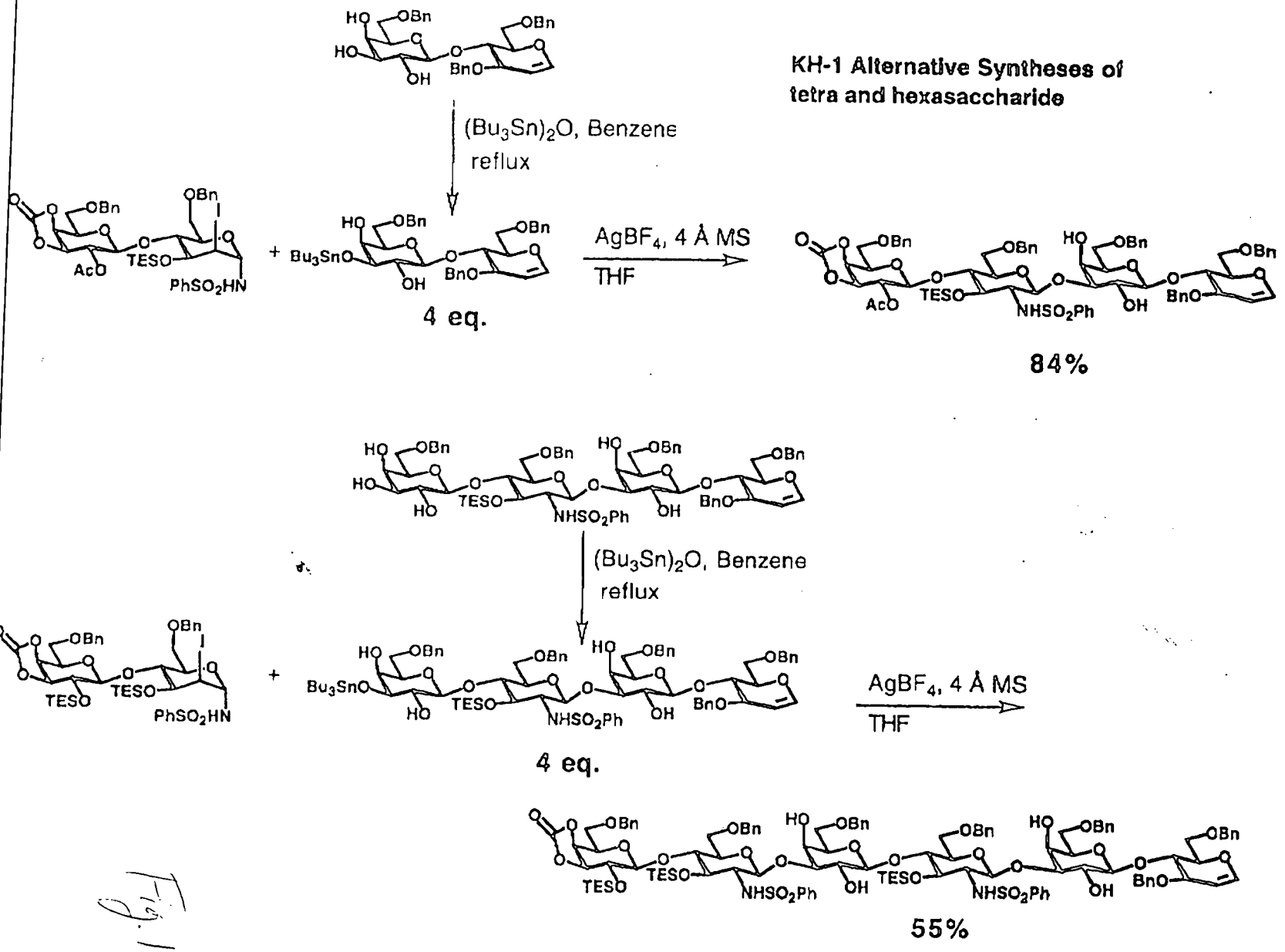
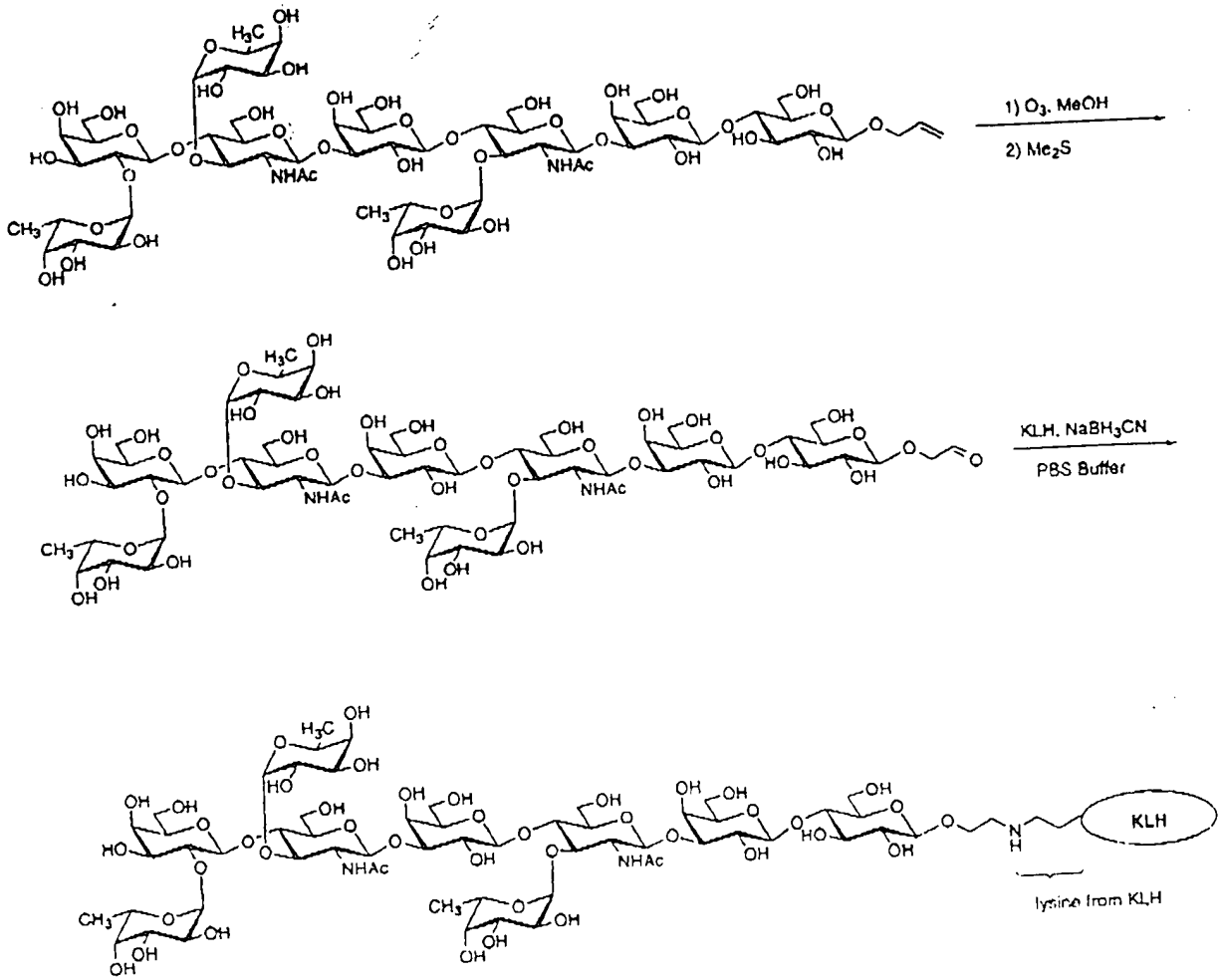
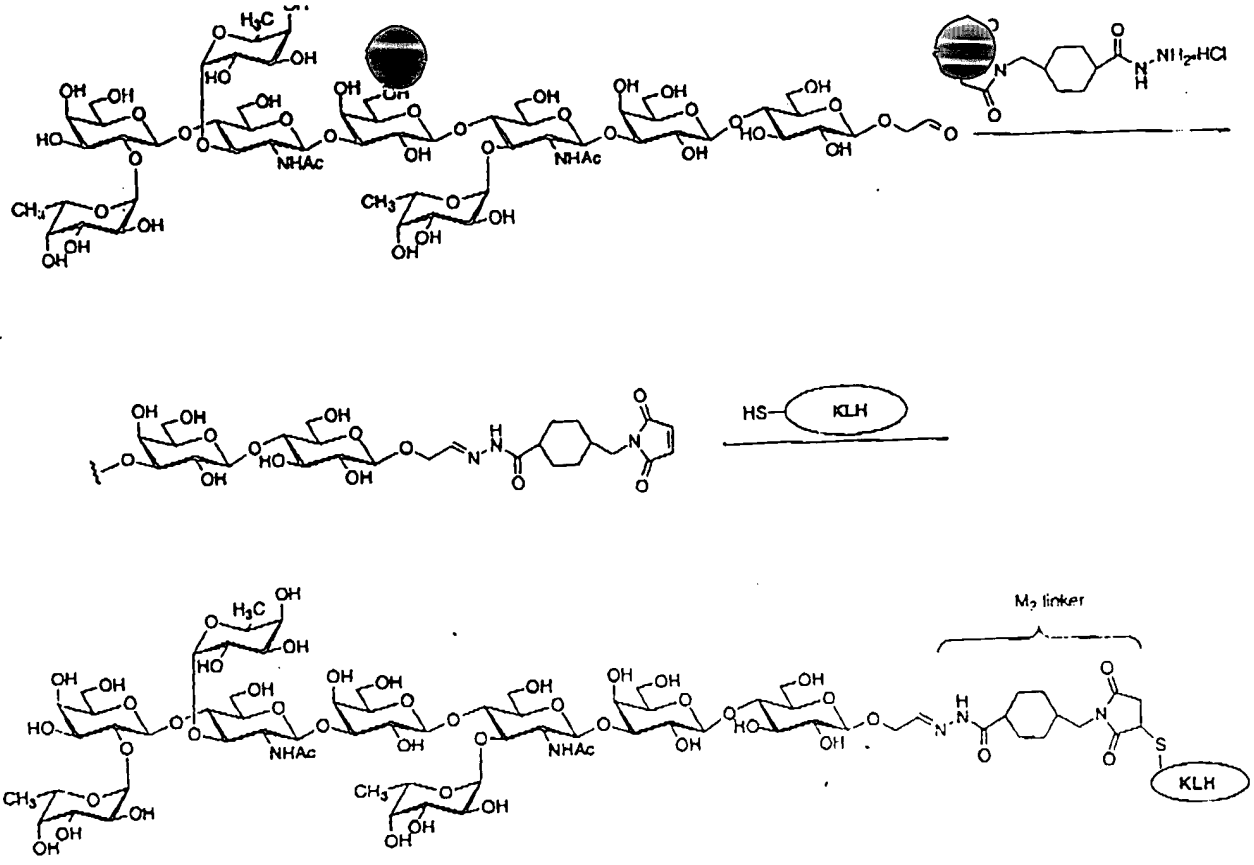
KH-1 Alternative Syntheses of tetra and hexasaccharide





Direct Coupling of KH-1 to KLH

Fig. 12



Cross linker coupling of KH-1 to KLH

Fig 13